(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. 199723934 B2
(10) Patent No. 727980

(54) Title
Wood glue incorporating an insecticide

(51)[6] International Patent Classification(s)
A01N 047/02 B27K 003/34
A01N 025/34 C08L 097/02
A01N 043/56 C09J 011/06
B27D 001/04

(21) Application No: 199723934 (22) Application Date: 1997 .04 .03

(87) WIPO No: WO97/37543

(30) Priority Data

(31) Number	(32) Date	(33) Country
96/04694	1996 .04 .09	FR
96/04695	1996 .04 .09	FR

(43) Publication Date : 1997 .10 .29
(43) Publication Journal Date : 1998 .01 .08
(44) Accepted Journal Date : 2001 .01 .04

(71) Applicant(s)
Rhone-Poulenc Agro

(72) Inventor(s)
Sylvestre Jobic

(74) Agent/Attorney
DAVIES COLLISON CAVE,1 Little Collins Street,MELBOURNE VIC 3000

(56) Related Art
JP 07-149606
WO 95/22902
EP 295117

OPI DATE 29/10/97 APPLN. ID 23934/97
AOJP DATE 08/01/98 PCT NUMBER PCT/FR97/00605
AU9723934
DEMA (PCT)

(51) Classification internationale des brevets 6 :
A01N 47/02, 43/56, 25/34, B27D 1/04, B27K 3/34, C09J 11/06, C08L 97/02 // (A01N 47/02, 25:34) (A01N 43/56, 25:34)

A1

(11) Numéro de publication internationale: WO 97/37543

(43) Date de publication internationale: 16 octobre 1997 (16.10.97)

(21) Numéro de la demande internationale: PCT/FR97/00605

(22) Date de dépôt international: 3 avril 1997 (03.04.97)

(30) Données relatives à la priorité:
96/04694 9 avril 1996 (09.04.96) FR
96/04695 9 avril 1996 (09.04.96) FR

(71) Déposant (*pour tous les Etats désignés sauf US*): RHONE-POULENC AGROCHIMIE [FR/FR]; 14/20, rue Pierre-Baizet, F-69009 Lyon (FR).

(72) Inventeur; et
(75) Inventeur/Déposant (*US seulement*): JOBIC, Sylvestre [FR/FR]; Le Perroux, F-69380 Alix (FR).

(74) Mandataire: PRAS, Jean-Louis; Rhône-Poulenc Agrochimie - DPI, 14/20, rue Pierre-Baizet, F-69009 Lyon (FR).

(81) Etats désignés: AU, BR, KR, US, brevet européen (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Publiée
Avec rapport de recherche internationale.

(54) Title: WOOD GLUE INCORPORATING AN INSECTICIDE

(54) Titre: COLLES A BOIS COMPRENANT UN INSECTICIDE

(57) Abstract

A wood glue containing a 1-(hetero)arylpyrazole-type active insecticide material and wooden materials bonded with a glue containing said active insecticide material are disclosed.

(57) Abrégé

Colle à bois comprenant une matière active insecticide de type 1-(hétéro)arylpyrazole et matériaux à base de bois collé par une colle comprenant cette matière active insecticide.

Wood adhesive comprising an insecticide

The present invention relates to the field of adhesives intended to bond wood and comprising an insecticide.

Adhesives intended for the bonding of wood or of wood particles are widely known.

These wood adhesives are generally of polymeric type, in particular based on thermoplastic or thermosetting polymers.

These wood adhesives are applied in many fields and in particular in the production of wood-based materials and more specifically wood-based materials of chipboard, plywood, laminate or veneer type and the like.

These materials are used in the construction of buildings, houses and blocks of flats, as well as in fitting out the said buildings, houses and blocks of flats, such as, for example, furniture.

Moreover, it is known that these materials are the subject of attacks by insects, in particular termites.

The prior art describes, especially in patent JP-7 149606, compositions for coating granules comprising an adhesive and an arylpyrazole-type insecticide. Documents WO-A-95/22902, EP-A-0,295,017, EP-A-0,500,209, DE-A-4,414,333 and WO-A-93/06089 describe insecticidal arylpyrazoles useful for the treatment of wood against termite attack.

There are also examples in the patent literature where a wood glue is mixed with an insecticide, such as patent JP-52 127936 in which the glue is used for gluing pieces of wood together.

Finally, examples of wood glues used in the manufacture of wood-based materials containing an insecticide of the organophosphorus, organochlorine or pyrethroid type are found in patents JP-3 047102, JP-59 227802, JP-62 016402, JP-5 036201, JP-8 039511 and JP-58 022107 and in the publication by R.H. BEAL *For. Prod. J.*, *29*(12), (1979), 29-34.

In point of fact, the number of products which can be used in practice for protecting wood against attacks by insects, in particular termites, is rather limited, all the more so since several of them have been dropped for reasons of environmental protection, such as, for example, the so-called organochlorinated products.

The need thus remains for wood adhesives conferring protection against insects, in particular termites, on materials based on bonded wood.

Advantageously, one or more embodiments of the invention may meet the existing requirements as regards adhesives comprising an insecticide which are involved in the manufacture of wood-based materials.

One or more embodiments of the invention may provide adhesives for the manufacture of wood-based materials which do not have the disadvantages of the known products.

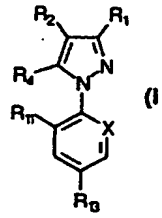
One or more embodiments of the invention may provide adhesives for the manufacture of wood-based materials which are resistant to insects, in particular to termites.

One or more embodiments of the invention may provide wood-based materials which are resistant to insects, in particular to termites.

One or more embodiments of the invention may provide wood-based materials of chipboard, plywood, laminate or veneer type which are immunized against perforations caused by insects.

The invention consequently relates to wood adhesives comprising an insecticidal active material of

formula (I):



(I

in which:

R_1 is CN or methyl;

R_2 is $S(O)_nR_3$;

R_3 is alkyl or haloalkyl;

R_4 represents a hydrogen or halogen atom or an NR_5R_6, $-S(O)_mR_7$, $-C(O)R_7$ or $-C(O)O-R_7$, alkyl, haloalkyl or $-OR_8$ radical or an $-N=C(R_9)(R_{10})$ radical;

R_5 and R_6 represent, independently of one another, the hydrogen atom or an alkyl, haloalkyl, -C(O)alkyl or $-S(O)_xCF_3$ radical or alternatively R_5 and R_6 can together form a divalent alkylene radical which can be interrupted by one or two divalent heteroatoms, such as oxygen or sulphur;

R_7 represents an alkyl or haloalkyl radical;

R_8 represents an alkyl or haloalkyl radical or the hydrogen atom;

R_9 represents an alkyl radical or the hydrogen atom;

R_{10} represents a phenyl or heteroaryl group optionally substituted by one or a number of halogen

atoms or groups such as -OH, -O-alkyl, -S-alkyl, cyano or alkyl;

R_{11} and R_{12} represent, independently of one another, a hydrogen or halogen atom;

R_{13} represents a halogen atom or a haloalkyl, haloalkoxy, $-S(O)_qCF_3$ or $-SF_5$ group;

m, n, q and r represent, independently of one another, an integer equal to 0, 1 or 2;

X represents a trivalent nitrogen atom or a $C-R_{12}$ radical, the other three valencies of the carbon atom forming part of the aromatic ring;

with the proviso that, when R_1 is methyl, then R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3 and X is N.

The term "alkyl" present in the definitions of the radicals of the compound of formula (I) represents a linear or branched alkyl radical containing from 1 to 6 carbon atoms.

The term "alkoxy" present in the definitions of the radicals of the compound of formula (I) represents a linear or branched alkoxy radical containing from 1 to 6 carbon atoms.

The term "alkylene" present in the definitions of the radicals of the compound of formula (I) represents an alkylene radical containing from 1 to 4 carbon atoms.

The term "halogen" and the prefix "halo-" present in the definitions of the radicals of the

compound of formula (I) mean respectively fluorine, chlorine, bromine or iodine and fluoro-, chloro-, bromo- or iodo-.

The term "heteroaryl" present in the definitions of the radicals of the compound of formula (I) represents an aromatic radical containing 5 or 6 atoms, one or a number among which can optionally be chosen from nitrogen, oxygen and sulphur.

A preferred class of compounds of formula (I) is composed of the compounds such that R_1 is CN and/or R_3 is haloalkyl and/or R_4 is NH_2 and/or R_{11} and R_{12} are, independently of one another, a halogen atom and/or R_{13} is haloalkyl.

A compound of formula (I) which is very particularly preferred in the present invention is 1-[2,6-Cl_2-4-CF_3-phenyl]-3-CN-4-[SO-CF_3]-5-NH_2-pyrazole, hereinafter known as Compound A.

Compounds of formula (I) can be prepared according to one or other of the processes described in Patent Applications WO-A-87/3781, WO-A-93/6089, WO-A-94/21606 or EP-A-295,117 or any other process coming within the competence of the person skilled in the art who is a specialist in chemical synthesis.

The invention consequently relates to wood adhesives containing an insecticide of formula (I).

In the present invention, wood adhesives is understood to mean adhesives, binding or bonding agents or glues intended for the bonding of wood, whether in

the form of sheets, laths, particles, and the like, to itself or to another substrate.

The wood adhesives which are used as base in the preparation of the wood adhesives containing an insecticide according to the invention are those known to the person skilled in the art and more particularly adhesives based on thermosetting resins and adhesives based on thermoplastic resins.

Adhesives based on thermosetting resins confer high mechanical strength on the materials and for this reason are more particularly used in the production of materials for furniture or frameworks.

Mention may be made, among adhesives based on thermosetting resins used in the present invention, without implied limitation, of urea-formaldehyde adhesives, phenol-formaldehyde adhesives, resorcinol-formaldehyde adhesives, melamine-formaldehyde adhesives and silicone adhesives.

By way of example, the phenol-formaldehyde adhesives will be used more particularly in the production of plywoods. Resorcinol-formaldehyde adhesives will be preferred, because of their excellent resistance to ageing and to weathering, for example for the manufacture of materials which can be used externally and/or which require a high guarantee of stability with respect to the weather.

Mention may be made, among adhesives based on thermoplastic resins, without implied limitation, of

vinyl adhesives and p lyacrylic adhesives.

A type of wood adhesive based on thermoplastic resin which is preferred for the present invention is composed of vinyl adhesives, for example vinyl resins, in particular poly(vinyl acetate), or, for example, adhesives based on acetochlorides, poly(vinyl alcohol), poly(vinyl acetal)s, poly(vinyl ether)s or vinyl acetate and more particularly adhesives based on ethylene-vinyl acetate copolymer.

Another category of adhesives to which the present invention relates is composed of elastomer-based adhesives.

The wood adhesives according to the invention can be composed of a single type of adhesive or of a mixture of adhesives (mixed adhesives).

The wood adhesives according to the present invention can be provided in the form of more or less viscous or pasty liquids, in the form of aqueous or alcoholic solutions, as emulsions, in the form of powders which are soluble in water or alcohol or in the form of films which can be applied directly. Finally, in the case of adhesives based on thermoplastic resins, these can be provided in the form of heat-fusible preparations.

The combined adhesives described above constitute a non-limiting list. It is clearly understood that any type of adhesive which is suitable for the bonding of wood is suitable for the present

invention. As a general rul , the choice of the wood adhesive will be determined by th p rson skilled in the art who is a specialist in the production of wood-based materials, according to the desired final application of the material.

The wood adhesives according to the invention are prepared by mixing a wood adhesive known per se with an effective amount of insecticidal active material of formula (I).

Effective amount of active material is understood to mean the amount of active material to be mixed with the adhesive so as to obtain wood-based materials which are effectively protected from attacks by insects.

These effective amounts of active material of formula (I) are amounts generally of between 0.5 and 150 g/l, preferably of between 5 and 50 g/l, of wood adhesive. When the wood adhesive according to the invention is packaged in the form of a powder, this is such that the wood adhesive, once in solution or emulsion, contains 0.5 to 150 g/l, preferably 5 to 50 g/l, of insecticidal active material of formula (I).

The invention also relates to wood-based materials composed of a plurality of flat layers of wood and/or of a plurality of wood particles bonded to one another by a wood adhesive comprising an insecticidal active material of formula (I).

In the materials of the invention, the

insecticidal active material is thus situated essentially in the adhesive, it being possible for this active material subsequently possibly to migrate in the wood-based material.

The materials based on wood bonded according to the invention are in particular materials based on chipboard, plywood, laminate and veneer.

The wood chipboard materials according to the invention have a thickness generally of between 5 and 100 mm, preferably between 7 and 80 mm.

By way of example, and depending on the final destination of the chipboard-based materials, the thickness will preferably be between 7.5 and 15 mm for the thinnest materials, between 10 and 40 mm for standard materials and between 35 and 80 mm for materials subjected to high stresses.

The particles capable of constituting the wood chipboard materials according to the invention are of a type known per se. They can in particular be fibres, flakes, slices, strips of the most varied lengths, specks, chips, parings, shavings, and the like.

These particles have a size generally varying from a few hundredths of a millimetre to 5 cm. More particularly, their size is advantageously between 0.1 mm and 3 cm, preferably between 0.1 cm and 2.5 cm.

The plywood materials according to the invention are composed of a plurality of flat layers,

preferably of 3 to 7 layers. The flat layers capable of constituting the plywood materials according to the invention are positioned with respect to one another so that their fibres are in general directions which cross each other and are even preferentially transverse with respect to one another, generally forming an angle of 90° between them.

Each of the layers has a thickness ranging from 0.5 mm to 2 cm, preferably from 1 mm to 1 cm.

These plywood-based materials can be composites, that is to say contain one or a number of layers of wood chipboard, of paper, of plastic film and the like coming in between the flat layers, or alternatively contain, on one of the faces or both faces, a solid wood or wood chipboard layer, which may or may not be decorative, or alternatively paper.

The final thickness of the plywood-based materials according to the invention is between 1 mm and 10 cm, preferably between 5 mm and 8 cm.

The different thicknesses, particle sizes, number of layers and the like presented above are given by way of information and should not be understood as limits from the viewpoint of the person skilled in the art.

The wood materials according to the invention are obtained in a way which is also known per se, in particular by hot or cold pressing of particles or flat layers with the adhesive, in the presence or absence of

a catalyst, according to techniques well known to the person skilled in the art. The type of adhesiv and its presentation are also chosen by the person skilled in the art according to the desired final destination of the bonded wood-based material.

According to the invention, the insecticidal active material is situated in this adhesive, which makes possible ready and simple manufacture of the products according to the invention, avoiding in particular the need to treat large volumes of material once in the finished or completed state.

The materials according to the invention are protected against attacks by insects, in particular against attacks of perforating type. As insects capable of generating such attacks, termites are one of the main agents.

The materials according to the invention are thus immunized against perforations originating from insects, in particular termites.

In addition to their immunity against perforations, the materials of plywood, laminate or veneer type according to the invention produce a barrier effect with respect to the passage of insects, in particular termites.

The amount of compound of formula (I) in the wood adhesives according to the invention is an amount which is effective in protecting the bonded wood-based materials against perforations.

These amounts which are effective for protection are amounts which confer on the materials concentrations of active material generally of between 0.05 and 15 g/m², preferably of between 0.5 and 5 g/m².

The following examples, given without implied limitation, illustrate the invention and show how it can be put into practice.

Example 1: Preparation of an insecticidal vinyl wood adhesive

An adhesive is prepared by mixing 10 g of the compound (A) with 1 litre of a wood adhesive based on ethylene-vinyl acetate copolymer. This crosslinkable adhesive is used directly in the production of wood chipboard or plywood.

Example 2: Preparation of an insecticidal melamine-formaldehyde wood adhesive

An insecticidal adhesive is prepared by mixing a powdered melamine-formaldehyde resin containing 25 g of active material (A) with 1 litre of water. This thermosetting resin can be used in the manufacture of plywood.

Example 3: Preparation of a chipboard

Wood chipboard is prepared by hot compression with the crosslinkable vinyl adhesive described in Example 1. The wood/adhesive ratio is such that the

wood chipboard material contains 1 g/m² of insecticidal active material (A).

A sheet of this wood chipboard with an area of 1 m² separates two chambers each comprising 200 termites with a choice of feeding and a water supply in order to ensure the survival, whatever happens, of the said termites.

After 21 days, it is observed that the sheet shows no signs either of perforation or of the beginning of perforation.

Example 4: Preparation of a plywood

Plywood is prepared by hot compression with the adhesive described in Example 2. The wood/adhesive ratio is such that the plywood material contains 1 g/m² of insecticidal active material (A).

A sheet of this plywood with an area of 1 m² separates two chambers each comprising 200 termites with a choice of feeding and a water supply in order to ensure the survival, whatever happens, of the said termites.

After 21 days, it is observed that the plywood sheet shows no signs either of perforation or of the beginning of perforation.

Example 5: Preparation of a laminate

Laminated wood is prepared by hot compression with the resin described in Example 2. The

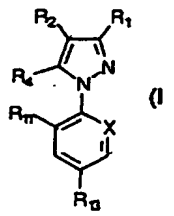
wood/adhesiv ratio is such that the laminated wood material contains 2.5 g/m^2 of insecticidal active material (A).

A sheet of this laminated wood with an area of 1 m^2 separates two chambers each comprising 200 termites with a choice of feeding and a water supply in order to ensure the survival, whatever happens, of the said termites.

After 21 days, it is observed that the laminated wood sheet shows no signs either of perforation or of the beginning of perforation.

CLAIMS

1. Wood adhesive comprising an insecticidal active material of formula (I):



(I)

in which:

R_1 is -CN or methyl;

R_2 is $-S(O)_aR_3$;

R_3 is alkyl or haloalkyl;

R_4 represents a hydrogen or halogen atom or an $-NR_5R_6$, $-S(O)_aR_7$, $-C(O)R_7$ or $-C(O)O-R_7$, alkyl, haloalkyl or $-OR_8$ radical or an $-N=C(R_9)(R_{10})$ radical;

R_5 and R_6 represent, independently of one another, the hydrogen atom or an alkyl, haloalkyl, -C(O)alkyl or $-S(O)_xCF_3$ radical or alternatively R_5 and R_6 can together form a divalent alkylene radical which can be interrupted by one or two divalent heteroatoms, such as oxygen or sulphur;

R_7 represents an alkyl or haloalkyl radical;

R_8 represents an alkyl or haloalkyl radical or a hydrogen atom;

R_9 represents an alkyl radical or a hydrogen

atom;

R_{10} represents a phenyl or heteroaryl group optionally substituted by one or a number of halogen atoms or groups such as -OH, -O-alkyl, -S-alkyl, cyano or alkyl;

R_{11} and R_{12} represent, independently of one another, a hydrogen or halogen atom;

R_{13} represents a halogen atom or a haloalkyl, haloalkoxy, $-S(O)_qCF_3$ or $-SF_5$ group;

m, n, q and r represent, independently of one another, an integer equal to 0, 1 or 2;

X represents a trivalent nitrogen atom or a $C-R_{12}$ radical, the other three valencies of the carbon atom forming part of the aromatic ring;

with the proviso that, when R_1 is methyl, then R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3 and X is N.

2. Wood adhesive according to claim 1, in which the active material of formula (I) is such that R_1 is CN.

3. Wood adhesive according to claims 1 or 2 wherein R_3 is haloalkyl.

4. Wood adhesive according to any one of claims 1 to 3 wherein R_4 is NH_2.

5. Wood adhesive according to any one of claims 1 to 4 wherein R_{11} and R_{12} are, independently of one another, a halogen atom.

6. Wood adhesive according to any one of claims 1 to 5 wherein R_{13} is haloalkyl.

7. Wood adhesive according to any one of the preceding claims, in which the active material of formula (I) is

1-[-2,6-Cl_2-4-CF_3-phenyl]-3-CN-4-[SO-CF_3]-5-NH_2-pyrazole.

8. Wood adhesive according to any one of the preceding claims, comprising an amount of product of formula (I) which is effective against insects.

9. Wood adhesive according to claim 8 wherein the insects are termites.

10. Wood adhesive according to one of the preceding claims, which is based on thermoplastic resin.

11. Wood adhesive according to claim 10, which is based on thermoplastic vinyl resin.

12. Wood adhesive according to one of claims 10 or 11, which is based on ethylene-vinyl acetate copolymer.

13. Wood adhesive according to any one of claims 1 to 4, which is based on thermosetting resin.

14. Wood adhesive according to claim 13, which is based on thermosetting phenol-formaldehyde resin.

15. Wood adhesive according to one of claims 13 or 14, which is based on resorcinol-formaldehyde resin.

16. Wood adhesive according to any one of the preceding claims, comprising an amount of product of formula (I) of between 0.5 and 150 g/l.

17. Wood adhesive according to claim 16 comprising an amount of product of formula (I) of between 5 and 50 g/l.

18. Wood-based material bonded with an adhesive comprising an amount of insecticidal active material of formula (I), as defined in any one of claims 1 to 7, which is effective against insects.

19. Wood-based material according to claim 18 wherein the insects are termites.

20. Wood-based material according to claims 18 or 19 composed of a plurality of wood particles bonded to one another by an adhesive comprising an insecticidal active material of formula (I) as defined in one of claims 1 to 7.

21. Wood based material according to claims 18 or 19, composed of a plurality of flat wood layers bonded to one another by an adhesive comprising an insecticidal active material of formula (I) as defined in one of claims 1 to 7.

22. Material according to any one of the preceding claims, comprising an amount of product of formula (I) as defined in one of claims 1 to 7 of between 0.05 and 15 g/m^2.

23. Material according to claim 22 comprising an amount of product of formula (I) of between 0.5 and 5 g/m^2.

24. Material according to any one of claims 18 to 22, based on wood bonded by an adhesive according to any one of claims 8 to 15.

25. Wood adhesive according to claim 1 substantially as hereinbefore described.

26. Wood-based material according to claim 18 substantially as hereinbefore described.

DATED THIS 17th day of October 2000

Rhone-Poulenc Agrochimie

by DAVIES COLLISON CAVE

Patent Attorneys for the Applicants